

Evaluation of Silicate Minerals for pH Control During Bioremediation: Application to Chlorinated Solvents

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Abstract Accurate control of groundwater pH is of critical importance for in situ biological treatment of chlorinated solvents. This study evaluated a novel approach for buffering subsurface pH that relies on the use of silicate minerals as a long-term source of alkalinity. A screening methodology based on thermodynamic considerations and numerical simulations was developed to rank silicate minerals according to their buffering efficiency. A geochemical model including the main microbial processes driving groundwater acidification and silicate mineral dissolution was developed. Kinetic and thermodynamic data for silicate minerals dissolution were compiled. Results indicated that eight minerals (nepheline, fayalite, glaucophane, lizardite, grossular, almandine, cordierite, and andradite) could potentially be used as buffering agents for the case considered. A sensitivity analysis was conducted to identify the dominant model parameters and processes. This showed that accurate characterization of mineral kinetic rate constants and solubility are crucial for reliable prediction

of the acid-neutralizing capacity. In addition, the model can be used as a design tool to estimate the amount of mineral (total mass and specific surface area) required in field applications.

Keywords Groundwater acidification · In situ bioremediation · Buffer injection · Geochemical modeling · Reductive dechlorination · Organohalide respiration

1 Introduction

Groundwater acidification of contaminated sites is a relatively frequent problem. The pH decrease can result from microbial processes (AFCEE 2004; Aulenta et al. 2006), presence of chemicals (like phenols or acid pesticides) and oxidative dissolution of sulfidic minerals, such as pyrite. Acidification is observed when the natural buffering capacity of ambient groundwater and soil is exceeded (McCarty et al. 2007; Robinson et al. 2009). Acidity buildup is of particular concern for in situ remediation processes such as bioremediation, chemical oxidation and reduction, and in situ mobilization–stabilization (Czupryna 1989; ITRC 2005; Robinson et al. 2009). For example, if the pH is too low reaction rates may be reduced or the solubility of the target chemical may be too high or too low. Consequently, the application of such techniques is enhanced by implementation of efficient pH-control strategies.

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In situ bioremediation of chlorinated aliphatic hydrocarbons (CAHs) is very sensitive to this issue (Adamson et al. 2004; Cope and Hughes 2001; McCarty et al. 2007). CAHs such as perchloroethylene (PCE) and trichloroethylene (TCE) are among the most frequently encountered subsurface contaminants due to their extensive use as dry cleaning and metal degreasing agents in many industrial processes (Fetzner 1998). CAHs are persistent in the environment and constitute a source of groundwater contamination that may last for decades (AFCEE 2004; McCarty et al. 2007). Enhanced in situ anaerobic bioremediation is a promising method to speed up their removal. It involves the stimulation of specialized anaerobic microorganisms that use chlorinated solvents as electron acceptors for energy metabolism through organohalide respiration (Yang and McCarty 2000, 2002). Stimulation of microbial activity is achieved by delivering an organic substrate into the subsurface, which is fermented to hydrogen, after which it is available as an electron donor for organohalide-respiring bacteria (ORB; AFCEE 2004). Organic substrate fermentation and organohalide respiration are both acid-producing processes, the extent of which is directly controlled by the amount of substrate and CAHs transformed (Adamson et al. 2004; AFCEE 2004; Amos et al. 2008; Chu et al. 2004). For this reason, source zone treatment is more susceptible to acidification than enhanced natural attenuation of dilute plumes due to the larger mass of CAHs available (Aulenta et al. 2006; Robinson et al. 2009).

Acidic conditions limit microbial degradation due to the inactivation of anaerobic bacteria at low pH. Pure strains of dehalogenating bacteria have a range of pH tolerance between 6–6.5 and 8–9.5 depending on the bacterial strain (Holliger et al. 1993; Krumholz 1997; Neumann et al. 1994; Scholz-Muramatsu et al. 1995; Sung et al. 2003; Suyama et al. 2001), while consortia are slightly more tolerant with a maximum pH range of 4–9 (Vainberg et al. 2009; Zhang and Bloom 1999). Fermenting bacteria exhibit a similar behavior with complete inhibition around pH 4–5 (Lee et al. 2002; Roychowdhury et al. 1988).

For field applications, the most common methods to control the pH decrease include the circulation of a solution containing dissolved alkaline materials (such as sodium or potassium bicarbonate) in the treatment zone (AFCEE 2004; Payne et al. 2006; Robinson et al. 2009) and the use of water injections to dilute the substrate and the acidity (Brovelli et al., Analysis of acidity production during enhanced reductive

dechlorination using a simplified reactive transport model, submitted). Constant addition of buffering agent requires frequent injections as alkalinity is rapidly consumed, which probably increases operation costs. In addition, in aquifers with significant concentrations of Ca^{2+} or Mg^{2+} , addition of bicarbonate may lead to precipitation of calcite at neutral pH (Lozecznik et al. 2010), which hinders further treatment.

The aim of this work was to assess the feasibility of an alternative strategy for pH control, which relies on the use of silicate minerals. Silicate minerals are the most common rock-forming mineral and their weathering is the predominant buffering mechanism in sediments with negligible carbonate content (Appelo and Postma 2005). The dissolution of silicates is accompanied by a release of alkali cations (such as K^+ , Na^+ , and Mg^{2+}) and by consumption of protons. Both processes can increase groundwater pH. Silicate minerals are appealing buffering agents as

- Dissolution is slow compared with carbonates, and therefore they are long-term sources of alkalinity (Appelo and Postma 2005)
- The dissolution rate is pH dependent, that is, minerals dissolve faster in acidic conditions (Marini 2007; White and Brantley 1995). This enhances their efficacy, as it allows a more rapid return to nearly neutral conditions while dechlorination is taking place, and increases their lifetime when the groundwater pH is in the neutral range
- The solubility is also pH dependent with a higher solubility at acidic pH and limited solubility at neutral pH.

In other words, when acidity is produced, minerals dissolve until a near-neutral pH is reached, then dissolution reduces due to thermodynamic constraints. This prevents the increase of groundwater pH in the alkaline range, which is as unfavorable to ORB as low pH.

Only a limited number of studies have evaluated the potential of silicate minerals as acid-neutralizing agents for water remediation. Silicate minerals resulting from industrial processes such as glass and ceramic production were considered, which contained sodium and potassium feldspars, nepheline, and wollastonite (Fernandez-Caliani et al. 2008; Kleiv and Sandvik 2000; Likens et al. 2004). In all cases, significant buffering capacity was observed and it was concluded that these materials can be used to mitigate water acidity and precipitate/stabilize heavy metals both in the soil (Kleiv

and Sandvik 2000) and streams (Fernandez-Caliani et al. 2008; Likens et al. 2004), resulting, for example, from acid mine drainage leaching. The studies conducted so far are, however, limited in the number of minerals and geochemical conditions considered. The objective of this study was to consider a larger spectrum of silicate minerals for acid neutralization than previous work. To this end, a screening methodology for the selection of the most suitable minerals was developed. The methodology was applied to the specific case of in situ bioremediation of chlorinated solvents, but can be extended to any decontamination technology requiring near-neutral pH conditions.

2 Methods

Silicate dissolution is primarily a surface process and its dissolution rate depends on the available specific reactive surface area (Appelo and Postma 2005; Marini 2007; White and Brantley 1995). Silicate minerals have different thermodynamic and kinetic characteristics and their dissolution rates vary over several orders of magnitude (Marini 2007). The methodology used to identify silicate minerals for pH control in the context of in situ bioremediation consists of three steps: (1) identification of silicate mineral kinetic parameters, (2) preselection based on thermodynamic considerations, and (3) numerical simulations to quantify and compare the buffering efficiency of the selected minerals.

A list of 20 silicates minerals was established (Table 1) and used as the starting point for the application of the screening methodology described in this work. These minerals were selected because (1) detailed studies on their dissolution kinetics were available in the literature, and (2) their thermodynamic parameters (solubility constant and enthalpy variation) were available and tabulated in existing geochemical databases. To limit the number of numerical simulations, silicate minerals with low reactivity, i.e., a slow dissolution rate in the acidic range (rate constant $<10^{-12}$ mol m⁻² s⁻¹) were excluded from the list.

2.1 Identification of Kinetic Parameters

The first step consists in determining the values of key parameters for mineral dissolution modeling, i.e., thermodynamic and kinetic parameters. Thermodynamic

parameters—such as solubility constant K_D and standard enthalpy of the reaction at 25°C ΔH —can normally be found in thermodynamic databases such as THERMOCALC (Blanc et al. 2007) and MINTQA2 (Allison et al. 1991; Table 1), whereas kinetic rates were not readily available. For a given temperature and at conditions far from equilibrium, the dissolution rate of most silicates can be expressed by the empirical rate law (White and Brantley 1995):

$$r = k_{H^+} (10^{-pH})^{-n_{H^+}} + k_W + k_{OH^-} (10^{-pH})^{-n_{OH^-}}, \quad (1)$$

where, r (mol m⁻² s⁻¹) is the dissolution rate, k_{H^+} , k_W , and k_{OH^-} (mol m⁻² s⁻¹) are the rate constants for the acidic, neutral and alkaline ranges, and n_{H^+} and n_{OH^-} are the reaction order of proton- and hydroxyl-promoted dissolution. Accurate determination of k_{H^+} , k_W , k_{OH^-} , n_{H^+} , and n_{OH^-} is critical for geochemical modeling. In order to estimate these values, published data from mineral dissolution experiments were fitted with Eq. 1.

For each mineral, two datasets taken from the literature were considered. Only experiments conducted in similar conditions were adopted, i.e., measurements from flow-through reactors, far from equilibrium conditions and at a temperature of 25°C. Moreover, only experiments where steady state conditions were achieved were considered. The estimated parameters (Table 2) were compared with those reported by Palandri and Kharaka (2004).

2.2 Mineral Screening Based on Thermodynamic Considerations

Of the 20 silicate minerals selected, a first screening was performed considering solubility. This property depends on the solubility constant, K_D , and on the ion activity product, which is related to proton activity and therefore to pH. The dependency of solubility upon pH is illustrated in Fig. 1 for five minerals (forsterite, wollastonite, nepheline, fayalite, and andradite). Solubility is high in the acidic range and decreases by several orders of magnitude with increasing pH. The relationship, however, differs among minerals. For pH control in the context of in situ CAH bioremediation, a good buffering agent should have high solubility in the acidic range (pH 4–6) and low solubility in the neutral-basic range (pH 7–9). High solubility for acidic conditions results in

Table 1 Dissolution reactions and thermodynamic parameters of the selected silicate minerals

Silicate mineral	Dissolution reaction	Log K_D ($T=25^\circ\text{C}$) ^a	ΔH [J mol ⁻¹] ^a
Albite	$\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} = \text{Al}^{3+} + \text{Na}^+ + 3\text{H}_4\text{SiO}_4$	4.14	-95,623
Almandine	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 12\text{H}^+ = 2\text{Al}^{3+} + 3\text{Fe}^{2+} + 3\text{H}_4\text{SiO}_4$	42.16	-465,683
Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 12\text{H}^+ = 3\text{Ca}^{2+} + 2\text{Fe}^{3+} + 3\text{H}_4\text{SiO}_4$	16.79	-137,101
Anorthite	$\text{Ca}(\text{Al}_2\text{Si}_2)\text{O}_8 + 8\text{H}^+ = 2\text{Al}^{3+} + \text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4$	25.31	-314,358
Chlorite	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 16\text{H}^+ = 5 \text{Mg}^{2+} + 2\text{Al}^{3+} + 3\text{H}_4\text{SiO}_4 + 6\text{H}_2\text{O}$	68.38 ^b	-634,275 ^b
Cordierite	$\text{Mg}_2\text{Al}_3(\text{AlSi}_5)\text{O}_{18} + 16\text{H}^+ + 2\text{H}_2\text{O} = 4\text{Al}^{3+} + 2 \text{Mg}^{2+} + 5\text{H}_4\text{SiO}_4$	49.41	-660,411
Diopside	$\text{CaMg}(\text{SiO}_3)_2 + 4\text{H}^+ + 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{H}_4\text{SiO}_4$	21.73	-158,241
Enstatite	$\text{MgSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$	11.83	-95,552
Fayalite	$\text{Fe}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Fe}^{2+} + \text{H}_4\text{SiO}_4$	19.02	-159,491
Forsterite	$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ = 2 \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$	28.60	-219,449
Glaucofane	$\text{Na}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2 + 14\text{H}^+ + 8\text{H}_2\text{O} = 2\text{Al}^{3+} + 3 \text{Mg}^{2+} + 2\text{Na}^+ + 8\text{H}_4\text{SiO}_4$	36.99	-397,394
Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 12\text{H}^+ = 2\text{Al}^{3+} + 3\text{Ca}^{2+} + 3\text{H}_4\text{SiO}_4$	49.36	-449,383
Jadeite	$\text{NaAl}(\text{SiO}_3)_2 + 4\text{H}^+ + 2\text{H}_2\text{O} = \text{Al}^{3+} + \text{Na}^+ + 2\text{H}_4\text{SiO}_4$	7.55	-100,168
Leucite	$\text{KAlSi}_2\text{O}_6 + 2\text{H}_2\text{O} + 4\text{H}^+ = 2\text{H}_4\text{SiO}_4 + \text{Al}^{3+} + \text{K}^+$	6.42 ^c	-92,465 ^c
Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3 \text{Mg}^{2+} + \text{H}_2\text{O} + 2\text{H}_4\text{SiO}_4$	32.56	-245,718
Nepheline	$\text{Na}(\text{AlSi})\text{O}_4 + 4\text{H}^+ = \text{Al}^{3+} + \text{Na}^+ + \text{H}_4\text{SiO}_4$	14.07	-146,839
Riebeckite	$\text{Na}_2(\text{Fe}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2 + 14\text{H}^+ + 8\text{H}_2\text{O} = 3\text{Fe}^{2+} + 2\text{Fe}^{3+} + 2\text{Na}^+ + 8\text{H}_4\text{SiO}_4$	-7.81	-18,281
Spodumene	$\text{LiAlSi}_2\text{O}_6 + 4\text{H}^+ = \text{Al}^{3+} + \text{Li}^+ + 2\text{H}_2\text{O} + 2\text{SiO}_2$	6.99 ^d	-89,181 ^d
Tremolite	$(\text{Ca}_2\text{Mg}_5)\text{Si}_8\text{O}_{22}(\text{OH})_2 + 14\text{H}^+ + 8\text{H}_2\text{O} = 2\text{Ca}^{2+} + 5 \text{Mg}^{2+} + 8\text{H}_4\text{SiO}_4$	67.25	-520,914
Wollastonite	$\text{CaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	14.02	-88,220

^a From THERMODDEM database except where indicated otherwise^b From PHREEQC database^c From MINTEQA2 database^d From LLNL database

a rapid return to neutral conditions while low solubility at high pH (>7) prevents excessive basification of the groundwater. Solubility in pure water of the 20 selected minerals was computed at pH 5 and 8 at a temperature of 20°C using the geochemical code PHREEQC-2 (Parkhurst and Appelo 1999) and solubility constants from the MINTEQA2, THERMODDEM and LLNL thermodynamic databases (provided with PHREEQC-2). Minerals with low solubility at pH 5 (<1 mmol l⁻¹) were excluded from the selection as they do not provide sufficient acid-neutralizing potential. Similarly, minerals with high solubility at pH 8 (above 10 mmol l⁻¹) were excluded, as they are likely to overshoot pH.

2.3 Numerical Model

In order to estimate the acid-neutralization potential of silicate minerals, a batch numerical model was

implemented using PHREEQC-2. The model included all relevant acid and alkalinity associated reactions occurring in chlorinated solvent-contaminated aquifers undergoing in situ bioremediation, i.e., mineral dissolution, microbial processes, and chemical speciation. The model was run in batch mode to simulate a well-stirred reactor. In this work, transport was neglected as it was assumed that groundwater residence time is large compared to the time scale of geochemical reactions.

2.3.1 Acid-Generating Processes

Two microbial processes are primarily responsible for groundwater acidification during CAH bioremediation: fermentation of the soluble organic substrate and organohalide respiration (McCarty et al. 2007; Robinson et al. 2009). In most in situ bioremediation schemes, dissolved hydrogen gas, the electron donor for ORB, is delivered through fermentation of an organic substrate

Table 2 Dissolution rate kinetic parameters of selected silicate minerals obtained by fitting Eq. 1 to literature datasets

Silicate mineral	Acid mechanism		Neutral mechanism	Basic mechanism		Reference of datasets
	Log k_{H^+} log (mol m ⁻² s ⁻¹)	n_{H^+}		Log k_{OH^-} log (mol m ⁻² s ⁻¹)	n_{OH^-}	
Albite	-11, -10.16	0.457, 1	-12.4, -12.56	-16.3, -15.6	-0.5, -0.572	Chou and Wollast (1984), Knauss and Wolery (1986)
Almandine	-5.2	1	-10.7	-13.71	-0.35	Sverdrup (1990)
andradite	-5.2	1	-10.7	–	–	Sverdrup (1990)
Anorthite	-8.2	0.55	-11.2	–	–	Berg and Banwart (2000), Hodson (2006)
Chlorite	-10.9, -9.79	0.25–0.49	-13	-16.79	-0.43	Brandt et al. (2003), Lowson et al. (2005)
Cordierite	-3.8	1	-11.2	–	–	Sverdrup (1990)
Diopside	-8.88, -9.46	0.28, 0.41	-11.21, -11.01	–	–	Knauss et al. (1993), Golubev et al. (2005)
Enstatite	-8.98, -9.02	0.24, 0.6	-12.72	–	–	Schott and Berner (1985), Oelkers and Schott (2001)
Fayalite	-5.9, -4.8	0.69, 1	-9.5	–	–	Sverdrup (1990), Wogelius and Walther (1992)
Forsterite	-6.78, -6.70	0.37, 0.74	-10.7, -10.1	–	–	Pokrovsky and Schott (2000), Golubev et al. (2005)
Glaucophane	-5.6	0.7	-10.1	–	–	Sverdrup (1990)
Grossular	-5.1	1	-10.7	–	–	Sverdrup (1990),
Jadeite	-8.82, -6	0.7, 0.72	-12, -9.5	-14	-0.3	Sverdrup (1990), Hamilton et al. (2001)
Leucite	-6	0.7	-9.2	–	–	Sverdrup (1990)
Lizardite	-5.7	0.8	-12.4	–	–	Sverdrup (1990)
Nepheline	-3.47	0.97	-8.61	–	–	Tole et al. (1986)
Riebeckite	-7.7	0.7	-12.2	–	–	Sverdrup (1990)
Spodumene	-4.6	0.7	-9.3	–	–	Sverdrup (1990)
Tremolite	-11.9, -8.4	0, 0.7	-12.5, -10.6	–	–	Mast and Drever (1987), Sverdrup (1990)
Wollastonite	-8.72, -7.13	0, 0.28	–	–	–	Weissbart and Rimstidt (2000), Golubev et al. (2005)

such as sodium lactate or linoleic acid,

organic substrate + wH_2O

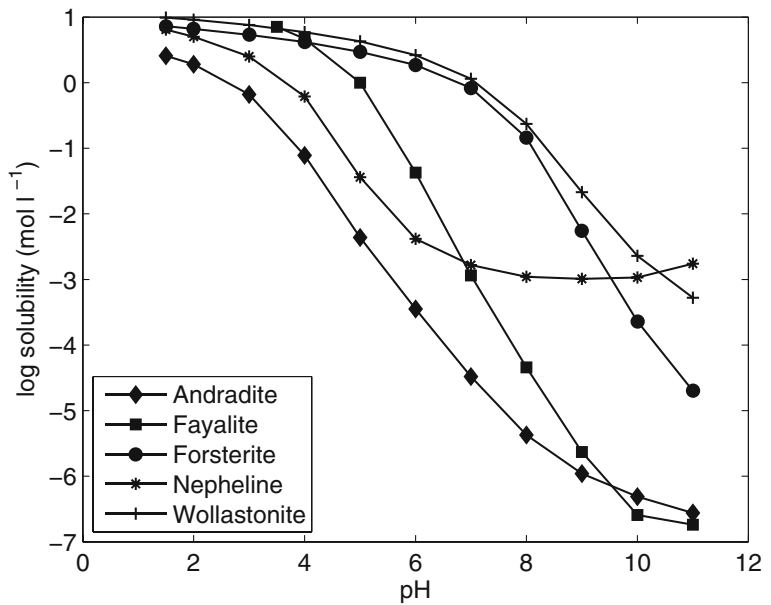
$$= xCH_3COOH + yH_2 + zCO_2. \quad (2)$$

The right-hand side of this equation lists the fermentation products, i.e., hydrogen, acetic acid, and carbon dioxide. The stoichiometric coefficients (w , x , y , z) are specific to the organic substrate used (Kouznetsova et al. 2010; McCarty et al. 2007; Robinson et al. 2009).

Not all hydrogen produced by fermentation is directed to organohalide respiration, as ORB must

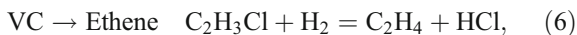
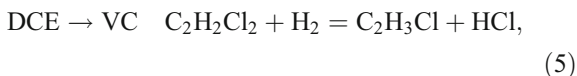
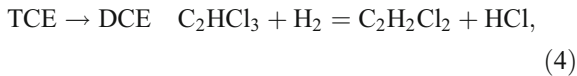
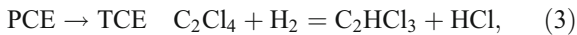
compete with other microbial guilds. In CAH source zones, sulfate and iron (III) are the two predominant competing terminal electron acceptors (AFCEE 2004; Aulenta et al. 2007). The fraction of hydrogen directed to ORB not only depends on the amount of iron oxides and sulfate present in the groundwater (AFCEE 2004), but also on microbial populations and specific field conditions and is therefore difficult to estimate precisely (Curtis 2003; Löffler et al. 1999). Following Robinson et al. (2009) and Robinson and Barry (2009), our model assumes that sulfate and iron oxide are present in excess in the system, and that a

Fig. 1 Influence of pH on solubility of five silicate minerals (andradite, fayalite, forsterite, nepheline and wollastonite). For all these minerals, solubility decreases with increasing pH



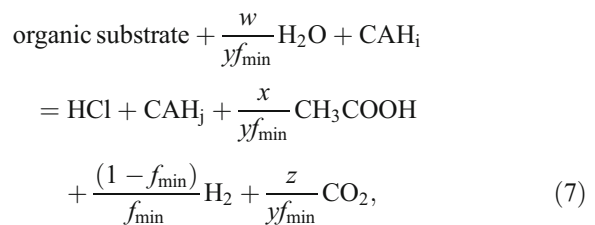
fraction f_{\min} of hydrogen produced by fermentation is used by ORB.

Organohalide respiration, i.e., reduction of PCE to ethene is modeled as a sequential reaction involving four steps,



where PCE stands for perchloroethylene, TCE for tetrachloroethylene, DCE for dichloroethene, and VC for vinyl chloride. If the reaction completes, for each mole of PCE degraded four moles of hydrochloric acid are produced. The goal of the model is to simulate the rate at which acidity is produced and not all complex microbial processes. Therefore, in order to simplify the model and reduce the computational burden, the fermentation rate is not simulated directly. Instead, the fermentation reaction is combined with organohalide respiration to give the following overall dechlorination

stoichiometry for each chloroethene (Robinson et al. 2009):



where, CAH_i and CAH_j are the parent and daughter CAHs, respectively.

The following assumptions were made regarding the fermentative and organohalide respiring bacterial guilds:

1. Fermentation is inhibited by high level of hydrogen, as shown by Fennell and Gossett (1998). The fermentation rate is, therefore, controlled by hydrogen consumption by organohalide respiration and by other anaerobic respiration processes
2. Acetate is not used as an electron donor. Robinson et al. (2009) demonstrated that acetate utilization as an electron donor lowers the overall acidity produced, so this represents the worst case in terms of acidity production
3. The concentration of fermentative biomass is high and remains constant
4. The impact of pH on microbial activity is similar for fermentative biomass and ORB

5. Sufficient organic substrate is provided to ensure complete transformation of the PCE to ethene
6. The organic substrate dissolution rate exceeds its fermentation rate

Organohalide respiration rates were modeled using Monod-type kinetic equations including competitive and Haldane inhibition (Cupples et al. 2004; Yu and Semprini 2004). The degradation rate of each chloroethene was computed as

$$R_{\text{PCE reduction}} = \frac{k_{\text{max,PCE}} X C_{\text{PCE}}}{K_{\text{S,PCE}} + C_{\text{PCE}}} f(\text{pH}), \quad (8)$$

$$R_{\text{TCE reduction}} = \frac{k_{\text{max,TCE}} X C_{\text{TCE}}}{K_{\text{S,TCE}} \left(1 + \frac{C_{\text{PCE}}}{K_{\text{Cl,PCE}}}\right) + C_{\text{TCE}} \left(1 + \frac{C_{\text{TCE}}}{K_{\text{HL,TCE}}}\right)} f(\text{pH}), \quad (9)$$

$$R_{\text{c-DCE reduction}} = \frac{k_{\text{max,c-DCE}} X C_{\text{c-DCE}}}{K_{\text{S,DCE}} \left(1 + \frac{C_{\text{TCE}}}{K_{\text{Cl,TCE}}}\right) + C_{\text{DCE}} \left(1 + \frac{C_{\text{c-DCE}}}{K_{\text{HL,c-DCE}}}\right)} f(\text{pH}), \quad (10)$$

$$R_{\text{VC reduction}} = \frac{k_{\text{max,VC}} X C_{\text{VC}}}{K_{\text{S,VC}} \left(1 + \frac{C_{\text{TCE}}}{K_{\text{Cl,TCE}}} + \frac{C_{\text{c-DCE}}}{K_{\text{Cl,c-DCE}}}\right) + C_{\text{VC}} \left(1 + \frac{C_{\text{VC}}}{K_{\text{HL,VC}}}\right)} f(\text{pH}), \quad (11)$$

and their temporal dynamics is

$$\frac{dC_{\text{PCE}}}{dt} = -R_{\text{PCE reduction}}, \quad (12)$$

$$\frac{dC_{\text{TCE}}}{dt} = R_{\text{PCE reduction}} - R_{\text{TCE reduction}}, \quad (13)$$

$$\frac{dC_{\text{c-DCE}}}{dt} = R_{\text{TCE reduction}} - R_{\text{c-DCE reduction}}, \quad (14)$$

$$\frac{dC_{\text{VC}}}{dt} = R_{\text{c-DCE reduction}} - R_{\text{VC reduction}}, \quad (15)$$

$$\frac{dC_{\text{ethene}}}{dt} = R_{\text{VC reduction}}, \quad (16)$$

where, C_j (mole per liter) is the aqueous concentration and $k_{\text{max},j}$ (moles per milligram protein per day) is the maximum specific utilization rate of CAH j (i.e., $j =$

PCE, TCE, DCE, and VC), X (milligram protein per liter) the dechlorinating biomass concentration and $K_{\text{S},j}$ (mole per liter) the half-saturation constant of each chloroethene j , $K_{\text{Cl},j}$ (mole per liter) is the competitive inhibition constant and $K_{\text{HL},j}$ the Haldane inhibition constant. $f(\text{pH})$ is a pH inhibition function that is described in detail below (Section 2.3.2).

Microbial growth is expressed as:

$$\frac{dX}{dt} = -Y \sum_{i=1,5} R_{j \text{ reduction}} - k_d X, \quad (17)$$

where, X (milligram protein per liter) is the biomass concentration, Y (milligram pro protein per mole per Cl released) is the growth yield coefficient, $R_{j \text{ reduction}}$ (mole per liter per day) is the reduction rate of CAH j and k_d (per day) is the first-order biomass decay rate. It was assumed that all ORB populations have the same yield coefficient and decay rate.

2.3.2 pH Inhibition Function

ORB is highly sensitive to groundwater pH. The dechlorination rate is maximal in the near-neutral range and decreases in the acidic and basic ranges. Several pH inhibition functions have been proposed to describe the pH influence on microbial activity (Bailey and Ollis 1986; Lee et al. 2002; Mussati et al. 2005; Schepers et al. 2002). In this study, the Gaussian-type function employed by Schepers et al. (2002) was used:

$$f(\text{pH}) = \exp \left[-\frac{(|\text{pH}_{\text{opt}} - \text{pH}|)^n}{\sigma^2} \right], \quad (18)$$

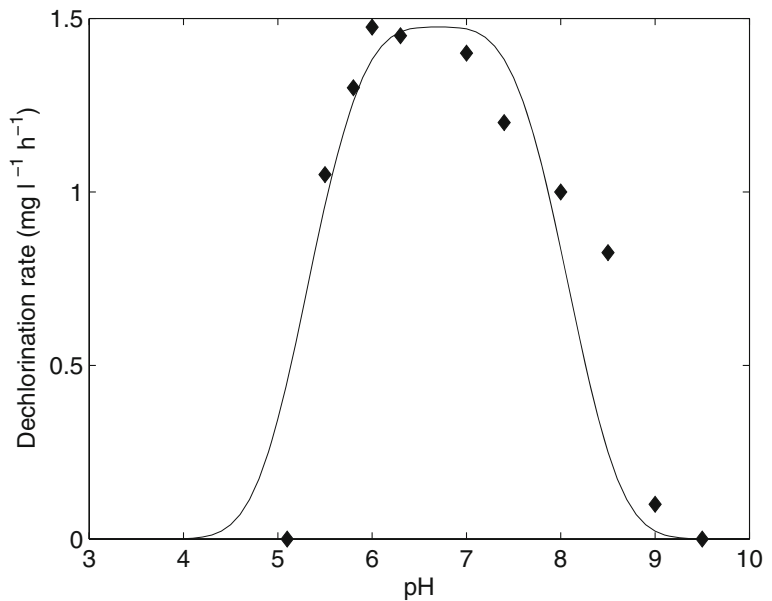
where, pH_{opt} (=6.7) is the optimal pH, and n and σ are empirical parameters that were estimated by fitting published datasets (Vainberg et al. 2009; Fig. 2).

2.3.3 Silicate Mineral Dissolution

Silicate mineral dissolution is a kinetically controlled process influenced by external factors such as temperature, pressure, pH, thermodynamic affinity, and water composition (Appelo and Postma 2005; Marini 2007). The general form of the rate law for mineral dissolution far from equilibrium proposed by Lasaga (1995) was adopted here:

$$R_D = r' \frac{A_0}{V} g(A)(1 - \Omega), \quad (19)$$

Fig. 2 pH versus dechlorination rate for a mixed organohalide respiring consortium. The filled diamonds represent the experimental data determined by Vainberg et al. (2009) and the line represents the fit of these data with Eq. 18



where, R_D (mole per liter) is the mineral dissolution rate, r' ($\text{mol m}^{-2} \text{s}^{-1}$) is the rate per unit surface area (given by Eq. 20), A_0 (square meter) is the initial surface area, V (l) is the solution volume, Ω (–) the mineral saturation index, $g(A)$ (–) is a function which quantifies the changes in reactive surface area as dissolution proceeds.

The rate per unit surface area r' is a function of temperature, pH, and groundwater composition and is expressed by:

$$r' = k_{H^+} \frac{(10^{-\text{pH}})^{-n_{H^+}}}{f_{H^+}} \exp \left[-\frac{E_{H^+}}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right] + \frac{k_W}{f_W} \exp \left[-\frac{E_W}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right] + k_{OH^-} (10^{-\text{pH}})^{-n_{OH^-}} \left[-\frac{E_{OH^-}}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right], \quad (20)$$

where, E_{H^+} , E_W and E_{OH^-} (Joules per mole) are the activation energies for the acid, neutral, and basic ranges, R (Joules per Kelvin per mole) the universal gas constant, T (Kelvin) the absolute temperature and f_{H^+} and f_W are factors accounting for inhibition by ionic species. The energy activation terms used in this study were taken from Palandri and Kharaka (2004) and are presented in Table 3. The effect of groundwater composition in the acidic and neutral ranges was

included through the inhibition factors f_{H^+} and f_W (Appelo and Postma 2005):

$$f_{H^+} = \left(1 + \frac{[\text{BC}]}{\text{Lim}_{\text{BC},H^+}} \right)^{x_{\text{BC}}} + \left(1 + \frac{[\text{Al}^{3+}]}{\text{Lim}_{\text{Al},H^+}} \right)^{x_{\text{Al}}}, \quad (21)$$

$$f_W = \left(1 + \frac{[\text{BC}]}{\text{Lim}_{\text{BC},W}} \right)^{z_{\text{BC}}} + \left(1 + \frac{[\text{Al}^{3+}]}{\text{Lim}_{\text{Al},W}} \right)^{z_{\text{Al}}}, \quad (22)$$

where, Lim is the threshold activity for solute inhibition, [BC] indicates the sum of activities of the base cations Na^+ , K^+ , and Mg^{2+} , $[\text{Al}^{3+}]$ is the activity of aluminum and exponents x_i and z_i are empirical parameters. The effect of CO_2 on the dissolution rate was not included as it is negligible for partial pressures up to 1 bar (Golubev et al. 2005). The coefficients Lim, x_i and z_i were determined for a limited numbers of minerals by Sverdrup and Warfvinge (1995) and Sverdrup (1990), and were adopted in this work. For most minerals, however, these values were not available. As discussed in Section 3.4.5, the model is only slightly sensitive to these inhibition factors, and therefore they can be neglected in the conditions selected in this study.

Table 3 Activation energy terms of silicate mineral dissolution in acid, neutral and basic range

Silicate mineral	Activation energy		
	E_{H^+} (kJ mol ⁻¹)	E_W (kJ mol ⁻¹)	E_{OH^-} (kJ mol ⁻¹)
Albite	65	69.8	71
Almandine	94.4	103.8	37.8
Andradite	94.41	103.8	n.d.
Anorthite	16.6	17.8	n.d.
Chlorite	88	88	88
Cordierite	113.3	28.3	n.d.
Diopside	96.1	40.6	n.d.
Enstatite	80	80	n.d.
Fayalite	94.4	94.4	n.d.
Forsterite	67.2	79	n.d.
Glaucofane	85	94.4	n.d.
Grossular	85	103.8	n.d.
Jadeite	132.2	94.4	n.d.
Leucite	132.2	75.5	56.6
Lizardite	75.5	56.6	n.d.
Nepheline	62.9	65.4	37.8
Riebeckite	56.6	47.2	n.d.
Spodumene	94.4	66.1	n.d.
Tremolite	18.9	94.4	n.d.
Wollastonite	54.7	54.7	n.d.

Data are from Palandri and Kharaka (2004)

n.d. not determined

The dissolution rate is also controlled by the available reactive surface area, which can change in time as the minerals dissolve (due, for example, to changes in the size and distribution of the crystal population, selective dissolution, aging of the mineral; Appelo and Postma 2005). In addition, precipitation of secondary mineral phases may coat the surface of the dissolving mineral (Gaus et al. 2008; Scislawski and Zuddas 2010). Reactive surface area is, however, not measurable. Also, it is difficult to correlate to the total surface area because, for instance, dissolution occurs only at certain sites on the mineral surface (Helgeson et al. 1984). Moreover, the reactive surface area might undergo variations of several orders of magnitude during dissolution (Brantley et al. 2008). Different models based on geometrical considerations have been proposed to relate changes in reactive surface area to mineral dissolution (Emmanuel and Berkowitz 2005;

Kieffer et al. 1999; Lichtner 1988). In this study, the approach of Lichtner (1988) was adopted,

$$g(A) = \left(\frac{m}{m_0} \right)^\alpha, \quad (23)$$

where, m_0 (mole) is the initial amount of mineral, m (mole) is the current amount of undissolved mineral and α is an exponent that depends on crystal shape, grain size distribution (Appelo and Postma 2005; Dixon and Hendrix 1993) and relative rates of dissolution on different surfaces (Witkamp et al. 1990). For a mono-disperse population of uniformly dissolving spheres or cubes $\alpha=0.67$, while $\alpha=3.4$ for a lognormal grain size distribution. Since this parameter is unknown and variable, $\alpha=0.67$ was arbitrarily chosen for the simulations conducted in this work and a sensitivity analysis was performed to assess its impact on model results.

Kinetic rate constants determined in laboratory experiments commonly exceed the mineral weathering rates observed in the field (White et al. 1996; White and Brantley 2003). Discrepancies were attributed to stirring in laboratory studies (Alkattan et al. 1998; Metz and Ganor 2001), inaccurate estimation of the mineral surface in aquifers (Brantley et al. 2008) and different characteristics of the mineral surfaces in the laboratory compared to field conditions (Davis and Hayes 1986). To correct dissolution rates obtained in the laboratory, following Vangrinsven and Vanriemsdijk (1992) a safety factor, D , was introduced,

$$R_D' = \frac{R_D}{D}, \quad (24)$$

where, R_D (moles per liter) is the total mineral dissolution rate obtained from continuous stirred flow reactor experiments and R_D' is the corrected value. Vangrinsven and Vanriemsdijk (1992) compared mineral dissolution rates in a number of different experiments and found $D \approx 15$ between dissolution rates determined in batch and in porous medium column experiments. This value was adopted in this work.

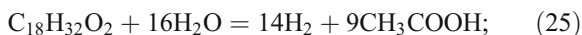
Precipitation of secondary minerals was not included due to the lack of a reliable modeling approach. Precipitation of a new mineral phase occurs when the saturation index exceeds a critical level, which is different for each mineral and in most cases is unknown (Zhu et al. 2010). Moreover, the definition of the initial surface area or of the nucleation sites is extremely difficult (Marini 2007; Zhu et al. 2010).

2.4 Numerical Simulations

2.4.1 Definition of Base Conditions

The model developed above was set up to simulate conditions of a typical groundwater undergoing in situ bioremediation. The conditions used were:

- The groundwater composition was defined using major constituents of a typical site contaminated with chlorinated solvents: K^+ , 0.2 mmol l^{-1} ; Mg^{2+} , 2.3 mmol l^{-1} ; Ca^{2+} , 7.2 mmol l^{-1} ; Na^+ , 5.9 mmol l^{-1} ; Cl^- 0.2, mmol l^{-1} ; SO_4^{2-} , 10.4 mmol l^{-1} ; CO_3^{2-} , 5.1 mmol l^{-1} ; pH, 6.8 (Kouznetsova et al. 2010)
- The temperature was set to 20°C: This value corresponds to the upper limit for groundwater temperature, which is usually between 10°C and 20°C (AFCEE 2004). This value was chosen because microbial rates are much higher at 20°C than at 10°C (Holliger et al. 1993; Zhuang and Pavlostathis 1995), consequently so is acidity production. In other words, this is the worst-case condition in term of acidity production
- The water was in equilibrium with a free phase of pure PCE (1.5 mmol l^{-1}). The solubility limit of PCE was set to 0.9 mmol l^{-1} (Yaws 1999)
- The factor f_{min} was set to 0.4, a typical value for field conditions (AFCEE 2004)
- The organic fermentable substrate used was linoleic acid, which is a major component of vegetable oil, a substrate often injected in field applications (AFCEE 2004). Linoleic acid is fermented to hydrogen and acetate following the reaction:



- The microbial kinetic parameters (maximum specific utilization rates, half-saturation constants, competitive and Haldane inhibition constants) were taken from Yu and Semprini (2004) for the PM culture, a mixed consortium able to convert PCE to ethene even at high PCE concentration. These kinetic parameters were determined at 20°C. All microbial processes model parameters used in the base case simulations are listed in Table 4
- It was assumed that the natural buffering capacity of soil and groundwater was already consumed, again this is the worst-case scenario

Table 4 Parameters for the microbial dechlorination model

Parameter and units	Value
Maximum degradation rates ($\mu\text{mol mg protein}^{-1} \text{ day}^{-1}$) ^a	
$k_{PCE,max}$	13.3
$k_{TCE,max}$	124
$K_{c-DCE,max}$	22
$k_{VC,max}$	2.4
Half velocity constants ($\mu\text{mol } l^{-1}$) ^a	
$K_{s,PCE}$	3.9
$K_{s,TCE}$	2.8
$K_{s,c-DCE}$	1.9
$K_{s,VC}$	602
Haldane inhibition constants ($\mu\text{mol } l^{-1}$) ^a	
$K_{HI,PCE}$	900
$K_{HI,c-DCE}$	6,000
$K_{HI,VC}$	7,000
Competitive inhibition constants ($\mu\text{mol } l^{-1}$) ^a	
$K_{CI,PCE}$	3.86
$K_{CI,TCE}$	2.76
$K_{CI,c-DCE}$	1.90
$K_{CI,VC}$	602.00
Biomass yields (mg protein/ $\mu\text{mol } Cl^-$) ^b	
Y	4.8×10^{-3}
First-order decay constant (day^{-1}) ^c	
k_d	2×10^{-2}
pH inhibition function parameters ^d	
n (—)	3.5
σ (pH units)	2.1
pH_{opt} (pH units)	6.7
Fraction of H_2 used for organohalide respiration (—) ^e	
f_{min}	0.35

^a Yu and Semprini (2004)

^b Maymo-Gatell et al. (1997)

^c Fennell and Gossett (1998)

^d Parameters fitted from data of Zhuang and Pavlostathis (1995)

^e Average value between 0.2 and 0.5 (AFCEE 2004)

Three cases were considered:

- Case A The pH was fixed at the optimal value for organohalide respiration (pH=6.7). The goal was to determine the time needed to complete degradation without pH inhibition.

- Case B This simulation was used to quantify the maximum dechlorination efficiency without addition of an external buffer.
- Case C In this simulation, fayalite was added to the system. The goal was to ascertain the effect on pH and therefore on PCE degradation efficiency. A total of 10 g of mineral with a specific surface area of $30 \text{ m}^2 \text{ g}^{-1}$ were used, using the formula defined by Borkovec et al. (1993), which incorporates the effect of surface roughness. This corresponds to a powder with grain size around $1.5 \text{ }\mu\text{m}$.

Results were analyzed considering the time required converting 99% of the initial PCE mass to ethene ($t_{99\%}$). This metric is directly linked to the buffering effect as the only parameter influencing the dehalogenation rate is pH: a rapid dechlorination (high $t_{99\%}$) reflects a good buffering capacity of the mineral. $t_{99\%}$ of case C above (named $t_{\text{BC},99\%}$) was used as a reference value in the sensitivity analysis.

2.4.2 Global Sensitivity Analysis

A global sensitivity analysis was conducted to ascertain the contribution of each parameter influencing mineral dissolution rate. This leads to identification of (1) insensitive parameters for model reduction and (2) sensitive parameters that require a more accurate characterization. The analysis also improved the understanding of the model behavior and clarified the interactions among parameters. For each parameter considered, the range of variability found in the literature was used: the model was run using the two extreme values while keeping the other parameters fixed. The description of all the cases and the values of the parameters used for the simulation are given in Table 5. Cases 1–5 focus on the influence of the mineral dissolution kinetic parameters k_{H^+} , k_{W} , k_{OH^-} , n_{H^+} , n_{OH^-} , E_{H^+} and E_{W} . The importance of the security factor D was investigated in case 6. The influence of the thermodynamic parameters K_{D} and ΔH was evaluated in cases 7 and 8, respectively. To get a better understanding of the model behavior, some parameters were evaluated together, in particular the kinetic rate constants k_{H^+} and k_{W} (case 2) and the

energy activation terms, E_{H^+} and E_{W} (case 5). In addition to model parameters, simulations were run to ascertain the effect of other important variables. The effect of temperature was evaluated in case 9 where the model was run for 10°C and 15°C . We considered also the inhibition of ionic species on mineral dissolution (case 10) and the representation of the reactive surface area changes (case 11). In this latter case, the parameter α was changed from 0.67 (uniform grain size distribution) to 3.4 (log normal distribution of the grains).

The $t_{\text{s},99\%}$ obtained from each run was compared to $t_{\text{BC},99\%}$ and the difference $\Delta t_{99\%} = t_{\text{s},99\%} - t_{\text{BC},99\%}$ was computed. A high $\Delta t_{99\%}$ indicates a marked contribution of the parameter to the model output and vice versa.

2.4.3 Mineral Ranking

The acid neutralizing potential and lifetime of the minerals selected during the preliminary screening were also quantified, considering the $t_{99\%}$ metric and the mass of mineral consumed per mole of PCE degraded. For each mineral, the appropriate thermodynamic and kinetic data were included in the model and are listed in Tables 1, 2 and 3. The same amount of mineral (50 mmol l^{-1} and surface area of 300 m^2 of mineral l^{-1} of solution) was considered in all simulations. The results were used to rank the minerals according to their suitability for field application as buffering agents.

3 Results and Discussion

3.1 Determination of Kinetic and Thermodynamic Parameters

Tables 1, 2, 3 report the results of the literature review conducted to collect the available kinetic and thermodynamic parameters for the 20 silicate minerals considered in this work. The stoichiometry of each dissolution reaction is also reported (Table 1), as it can be used to quantify the buffering potential of each mineral through the number of protons consumed per mole of dissolution. This value varies among the minerals, from 16 moles of protons per mole of dissolved mineral (cordierite, chlorite) to 2 moles of protons per mole of dissolved mineral (enstatite, wollastonite).

Table 5 Result of global sensitivity analysis

Case	Parameters	Units	Base case value	Sensitivity value		
1	$\log k_{\text{OH}^-}$	\log ($\text{mol m}^{-2} \text{s}^{-1}$)	BC value –	Case 1.1	Case 1.2	
	Results			–16.3	–13.7	
	$t_{s99\%}$			25	25	
	$\Delta t_{99\%}$			0	0	
2	$\log k_{\text{W}}$	\log ($\text{mol m}^{-2} \text{s}^{-1}$)	–5.35	Case 2.1	Case 2.2	Case 2.3
	$\log k_{\text{H}^+}$			–4.85	–5.85	–6.35
	Results			–9	–10	–10.5
	$t_{s99\%}$			17	52.3	Not reached
	$\Delta t_{99\%}$			–8	27.3	–
3	n_{H^+}	–	BC value 0.85	Case 3.1	Case 3.2	
	Results			0.28	1	
	$t_{s99\%}$			17	30.6	
	$\Delta t_{99\%}$			–8	5.6	
4	n_{OH^-}	–	BC value 0.85	Case 4.1	Case 4.2	
	Results			0	1	
	$t_{s99\%}$			25	25	
	$\Delta t_{99\%}$			0	0	
5	E_{W}	kJ mol^{-1}	BC value 94.4	Case 5.1	Case 5.2	
	E_{H^+}			51	104	
	Results			18.9	132	
	$t_{s99\%}$			24.8	27.7	
	$\Delta t_{99\%}$			–0.2	2.7	
6	Security factor D	–	BC value 15	Case 6.1	Case 6.2	
	Results			1	50	
	$t_{s99\%}$			17	54.6	
	$\Delta t_{99\%}$			–8	29.6	
7	Solubility constant K_{D}	–	BC value 19.02	Case 7.1	Case 7.2	Case 7.3
	Results			–7.8	68.4	1
	$t_{s99\%}$			Not reached	17	43
	$\Delta t_{99\%}$			–	–8	18
8	Standard enthalpy ΔH	J mol^{-1}	BC value 159 491	Case 8.1	Case 8.2	
	Results			88 220	1 965 817	
	$t_{s99\%}$			25	25	
	$\Delta t_{99\%}$			0	0	

Table 5 (continued)

Case	Parameters	Units	Base case value	Sensitivity value	
9	Temperature	°C	BC value	Case 9.1	Case 9.2
	Results		20	10	15
	$t_{s99\%}$			62.9	36.4
	$\Delta t_{99\%}$			37.9	11.4
10	Ionic species inhibition f_{H^+}/f_W		BC conditions	Case 10.1	
	lim BC	–	$f_{H^+}=1, f_W=1$	200	
	xBC			0.3	
	Results				
	$t_{s99\%}$			29	
	$\Delta t_{99\%}$			4	
11	Surface area evolution α	–	0.67	Case 11.1	
	Results			3.4	
	$t_{s99\%}$			26.9	
	$\Delta t_{99\%}$			1.9	

Case-specific parameters/conditions used and value of $t_{s99\%}$ and $\Delta t_{99\%}$

Mineral dissolution kinetic parameters identified using Eq. 1 are listed in Table 2. For most minerals, the dissolution parameters in the alkaline range (k_{OH^-} and n_{OH^-}) could not be determined as most studies only considered the acid-neutral range. Even though the datasets considered were produced from experiments in similar conditions, large differences between them were found. These led to uncertainties in the determination of the parameters as large as 3 orders of magnitude for k_{H^+} and 2 orders of magnitude for k_W . These large ranges are likely due to one or more of the following: uncertainties in estimates of the available reactive surface area (Aagaard and Helgeson 1982; Gautier et al. 2001; Helgeson et al. 1984), differences in the experimental design and solid phase preparation such as stirring rate (Metz and Ganor 2001), grinding method, or differences in the initial structure and composition of the mineral (Palandri and Kharaka 2004). When datasets for the same mineral were significantly different, a range of values was determined (Table 2). As an illustration, Fig. 3 shows the results of the fit for the mineral diopside. Two datasets were used (Golubev et al. 2005; Knauss et al. 1993) to determine the kinetic parameters. Fitting of the parameters was done for each dataset. As a result, two values were obtained for each parameter and the upper

and lower limits of the kinetic equation were computed (Fig. 3).

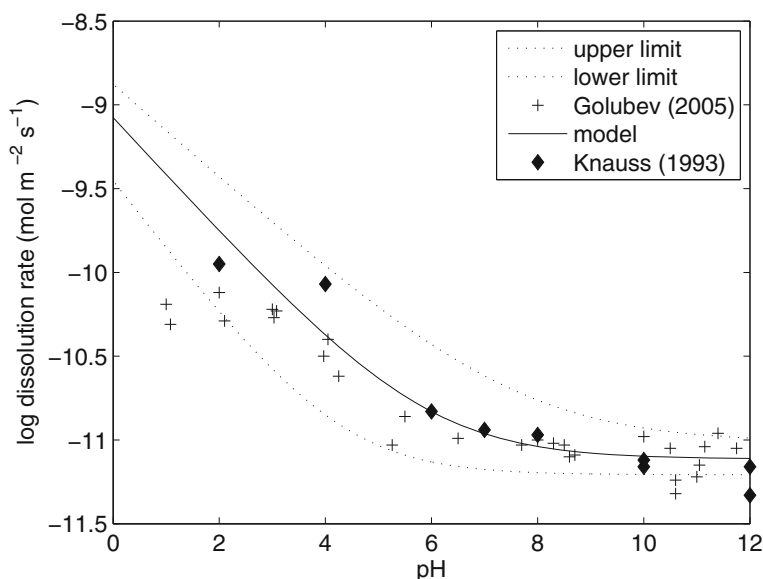
All minerals considered have a pH-dependent dissolution rate with the reaction order of proton-promoted dissolution n_{H^+} between 0.14 and 1 (average value). Comparison of kinetic parameters showed high variability. In the acidic range, the kinetic constant k_{H^+} varies over 7 orders of magnitude, the fastest and slowest minerals being nepheline and albite. The kinetic constant in the neutral range k_W shows a slightly smaller variation (4 orders of magnitude between nepheline and albite).

The kinetic constants determined in this work fall in the range reported by Palandri and Kharaka (2004) for the majority of the minerals. A mismatch was found in seven cases, and was attributed to different criteria used to select the datasets. In particular, in contrast to the compilation of Palandri and Kharaka (2004), in this study only datasets using a similar experimental setup and conditions were considered.

3.2 Mineral Screening Based on Thermodynamic Considerations

The values of the solubility in the acid range at pH 5 and in the basic range at pH 8 are presented in Fig. 4.

Fig. 3 Diopside dissolution rate versus pH. The points represent the data obtained by Golubev et al. (2005) and Knauss et al. (1993). The lines were obtained by fitting these datasets to Eq. 1. For each dataset, a different value of the three parameters k_{H^+} , n_{H^+} and k_W was obtained. Therefore, two values were available for each parameter. The continuous line was computed with the average value while the dotted lines were computed with the minimal and maximal values



Minerals with a solubility higher than 10 mmol l^{-1} are likely to lead to an increase of pH above 9, which is inhibitory to ORB (Vainberg et al. 2009; Zhuang and Pavlostathis 1995) and therefore they were excluded. On the other hand, in the acidic range solubility should

be sufficient to avoid limitation of mineral dissolution due to thermodynamic constraints. The minerals selected present a wide range of solubility at pH 5 and 20°C ranging from 4.3 mol l^{-1} for wollastonite to $8.45 \times 10^{-5} \text{ mol l}^{-1}$ for riebeckite. All minerals with

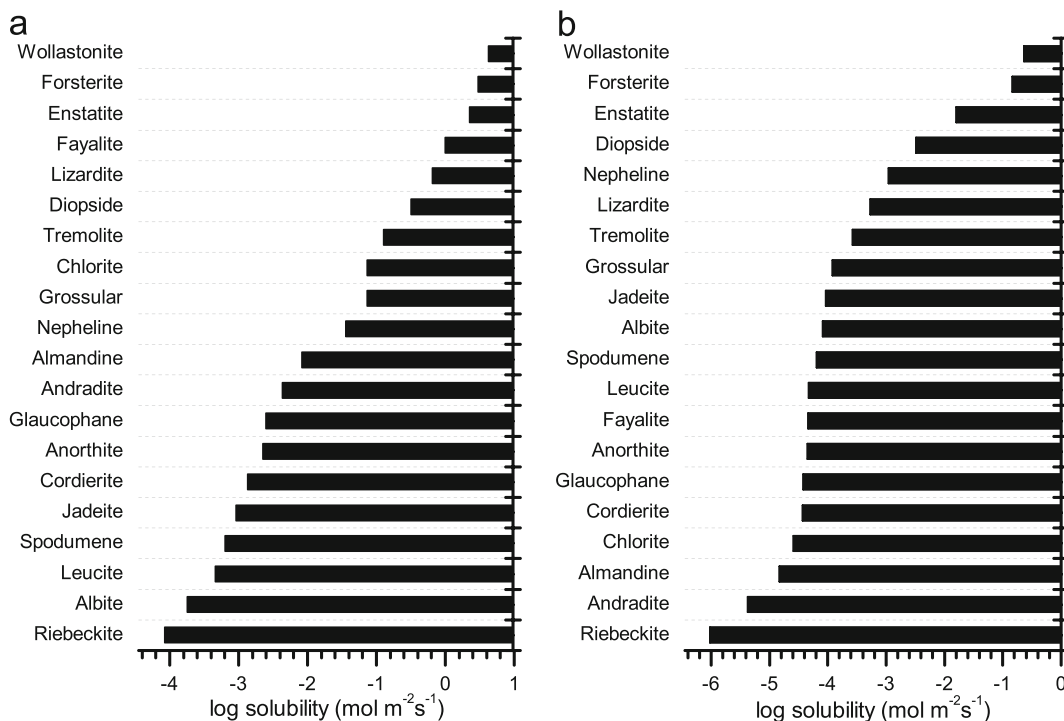


Fig. 4 Logarithm of mineral solubility at pH 5 (a) and pH 8 (b) for the 20 selected silicate minerals. These solubility values were calculated at 20°C in pure water. The solubility values vary by several orders of magnitude among minerals

Table 6 Mineral classification based on the solubility constant in acid and alkaline conditions

Class 1 Excessive solubility at pH 8	Class 2 Insufficient solubility at pH 5	Class 3 Appropriate solubility at pH 5 and 8
Forsterite	Riebeckite	Cordierite
Wollastonite	Albite	Anorthite
Enstatite	Leucite	Glaucophan
	Spodumene	Andradite
	Jadeite	Almandine
		Nepheline
		Grossular
		Chlorite
		Tremolite
		Diopside
		Lizardite
		Fayalite

Minerals belonging to class 1 have a solubility at pH 8 in excess of 10 mmol l^{-1} , while minerals belonging to class 2 have a solubility at pH 5 below 1 mmol l^{-1} . Minerals from the third class have a suitable solubility to be used as buffering agent (solubility above 1 mmol l^{-1} at pH 5 and below 10 mmol l^{-1} at pH 8)

solubility lower than 1 mmol l^{-1} were excluded. Minerals were classified in three classes according to their change in solubility as a function of pH (Table 6).

3.3 Base Simulations

Base simulations demonstrated the positive impact of the addition of silicate mineral on groundwater pH and on the activity of ORB. If the influence of pH on dechlorination is neglected, degradation of 99% of 1.5 mmol l^{-1} of PCE to ethene occurs in 17 days ($t_{99\%}$) with transient accumulation of VC and to a smaller extent of DCE and TCE (Fig. 5a). Until day 2, the PCE concentration is equal to 0.9 mmol l^{-1} (PCE solubility). After 2 days, the separate PCE phase was dissolved and the aqueous PCE concentration started to decrease.

When the feedback of pH on ORB activity is considered, without an external source of alkalinity, the pH dropped below 4.5 after 9 days, stopping the dechlorination (Fig. 5b). Degradation of PCE was incomplete and, after 18 days, only 64% of the initial mass was transformed to DCE and VC. When dechlorination ceased, 4.6 mmol of acetate and 2.7 mmol of

hydrochloric acid had been produced, indicating that the two processes contribute in a similar extent to groundwater acidification. This simulation highlights the need of an external buffer during enhanced bioremediation of CAHs when the natural soil buffering capacity is small.

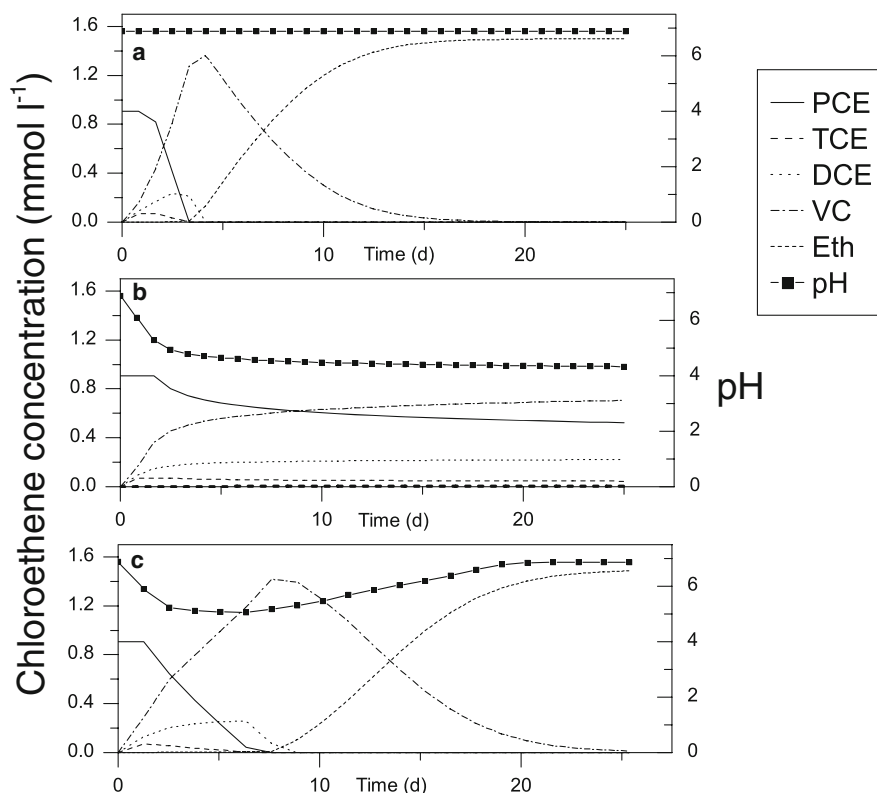
The addition of fayalite had a positive impact on the CAHs degradation rates, with $t_{99\%}=25$ days (Fig. 5c). The pH initially dropped to 5.1 due to rapid conversion of PCE to VC because dechlorination was faster than mineral dissolution. Afterwards, the pH returned close to neutral as the transformation of VC to ethene is slower than the previous dechlorination steps (see maximum degradation rates in Table 4) and because acidic conditions further reduced the activity of ORB. At the end of the simulation, 7 mmol of fayalite were consumed. When CAH removal was completed, the pH remained stable at 6.87 and mineral dissolution ceased since solubility of fayalite is very low at neutral pH (Fig. 1). This simulation suggested that, for the conditions considered, fayalite is a good candidate for groundwater buffering as pH remains close to neutral. Moreover, only the quantity required to buffer the acidity produced was used, and the rest remained in the system. This suggests that fayalite is also a good long-term source of alkalinity.

3.4 Global Sensitivity Analyses

3.4.1 Influence of Mineral Dissolution Rate Parameters

The results of the global sensitivity analysis are presented in Table 5. The kinetic rate parameters in the alkaline range (k_{OH^-} and n_{OH^-}) have no influence on the degradation rate ($\Delta t_{99\%}=0$, cases 1 and 4). The reason is that water remains in the acid-neutral pH range for the entire simulation period. Therefore, the lack of available data for these parameters does not limit model application. Conversely, k_{H^+} and k_{W} have a significant impact on the model response. A fivefold decrease of k_{H^+} and k_{W} (case 2.2) increased $t_{99\%}$ to 52.3 days (twice as long as the base case). When these two parameters were an order of magnitude smaller than in the base case (case 2.3), 99% degradation of PCE was not achieved. Hence, k_{H^+} and k_{W} directly control the mineral dissolution rate: When they are too low compared with the CAH degradation rate, the pH drops rapidly inhibiting bacterial activity. Similarly,

Fig. 5 Dechlorination pattern and pH evolution for the case A (pH constant at its optimal value) (a), case B (pH inhibition) (b) and case C (introduction of $300 \text{ m}^2 \text{ l}^{-1}$ of fayalite) (c)



the security factor D has a significant impact on the model output (case 6). An increase of D from 15 to 50 increased $t_{99\%}$ by 29.6 days.

3.4.2 Influence of Activation Energy

The influence of the activation energy terms E_{H^+} and E_W on the model response is very limited. E_{H^+} was varied between 18.9 and 132 kJ mol^{-1} and E_W between 51 and 104 kJ mol^{-1} , corresponding to the minimum and maximum values observed for the 20 selected minerals (case 5). The resulting $\Delta t_{99\%}$ was equal to -0.2 days (minimal values of the activation energy) and 2.7 days (maximal values of activation energy). Activation energy controls the changes in the mineral dissolution rate when temperature is different from 25°C . The simulations reported here considered a temperature of 20°C fairly close to the reference value, which partially explains the weak sensitivity. Further numerical simulations with lower temperatures (e.g., 10°C) indicated that, for typical groundwater temperatures, the influence of activation energies remains limited.

3.4.3 Influence of Solubility Constant

Riebeckite has the smallest solubility constant among the minerals considered ($\log K_D = -7.81$). For this value (case 7.1), the target 99% PCE degradation is not reached as the solution rapidly equilibrates with the mineral phase and dissolution halts. Only a total of 0.16 mmol of mineral dissolved within 25 days (compared to 7 mmol l^{-1} for the base case). Conversely, an increase of the solubility constant up to 68.4 (value for chlorite) reduced $t_{99\%}$ to its minimum value, i.e., 17 days (case 7.2), which corresponds to an optimal pH over the entire simulation period. In this case, the solution always remained far from equilibrium with the mineral phase and mineral dissolution was only controlled by kinetics.

3.4.4 Influence of Temperature

A 10°C decrease in temperature increased $t_{99\%}$ to 62.9 days (2.5-fold increase; case 9.1). In the simulations, temperature changes affect the mineral

dissolution rates and solubility constants. The influence of temperature on the dechlorination rate was instead not taken into account and the same parameters for biological transformations estimated at 20°C were used. The reason for this approximation was the lack of information about the extent of reduction of the dechlorination rate with temperature for the PM consortium. Zhuang and Pavlostathis (1995) studied the influence of temperature on a ORB mixed culture and showed that the rate was approximately halved reducing the temperature from 20°C to 15°C. On the other hand, a change in ambient temperature from 20°C to 15°C leads to a decrease of the mineral dissolution rate of fayalite by a factor of 1.8 (Eq. 20). This suggests that, in the temperature range 10–20°C, the change in dechlorination rate will be similar to the change in dissolution rate and buffering capacity of the mineral, with little or no effect on the ability of the mineral to counterbalance the acidity produced. The $t_{99\%}$ value will increase nevertheless, as the rate at which CAHs are transformed is reduced at lower temperatures.

3.4.5 Cation Inhibition Function

The goal of case 10 was to evaluate the importance of the base cations inhibition terms f_{H^+} and f_W in Eq. 20. As discussed previously, these parameters are available for few minerals only and it was therefore important to ascertain the resulting error on model predictions. For the groundwater composition considered in this simulations, the decrease in dechlorination efficiency when the inhibition terms are considered is relatively small, $\Delta t_{99\%}=4.4$ days. This value should be compared with that resulting from the uncertainty in the kinetic rate parameters k_{H^+} and k_W , which is five or more times larger ($\Delta t_{99\%}>20$ days). As a result, the two inhibition terms can be neglected for the conditions used. For higher concentrations of Al^{3+} , Na^+ , K^+ , and Mg^{2+} , this choice should be tested further. For example, additional calculations showed that, for the case where the sum of the activities of the base cations exceeds 20 mmol l^{-1} , the dissolution rate of K-feldspar is halved.

3.4.6 Surface Area Evolution

Case 11 investigated the effect of changing the parameter α in Eq. 23, that is, the equation governing the change in reactive surface area as mineral dissolution

proceeds. The parameter was changed from 0.67—which corresponds to a monodisperse population of spherical grains—to 3.4, the value for a lognormal grain size distribution. Simulation results showed a $\Delta t_{99\%}=1.9$ day. It was then concluded that this parameter has little influence, and uncertainties in its determination introduce only a small change in simulation results.

3.4.7 Summary of Global Sensitivity Analyses

Results of global sensitivity analyses demonstrated that the most influent parameters are the solubility constant, K_D , and the kinetic dissolution rate constants in the acidic and neutral range k_{H^+} and k_W . The security factor D also influenced significantly the model response. Experimental determination of the kinetic rate constants is associated with a high level of uncertainty as discussed before. Therefore, additional efforts should be spent to characterize better those parameters, in particular in field conditions. With current knowledge, this method can still be successful but it might be necessary to overestimate the amount of mineral to be injected, to guarantee sufficient buffering capacity.

3.5 Comparison among Minerals

Additional simulations were used to rank the 12 minerals previously selected on the basis of their solubility

Table 7 Results of the screening methodology

Silicate mineral	$t_{99\%}$	Grams of mineral per mmol of PCE transformed
Nepheline	21	0.54
Fayalite	24.8	0.97
Glaucophane	29.8	0.51
Lizardite	29.8	0.45
Grossular	35	0.50
Almandine	46.8	0.74
Cordierite	48.6	0.32
andradite	53.8	0.49
Anorthite	Not reached	—
Chlorite	Not reached	—
Diopside	Not reached	—
Tremolite	Not reached	—
Enstatite	Not reached	—

Nepheline has the smallest $t_{99\%}$ and is therefore the best candidate as buffering agent

in the acid/alkaline pH range (i.e., those belonging to class 3 in Table 6). The minerals were ordered considering the time required to reach 99% degradation of the initial PCE mass, i.e., the more suitable minerals had lower $t_{99\%}$ values. Results are reported in Table 7. Of the 12 minerals tested, five (anorthite, chlorite, diopside, tremolite, and enstatite) had a dissolution rate that was too low to counterbalance acidity produced by the dechlorination. As a result, the target 99% PCE degradation was not reached and byproducts (mainly vinyl chloride) accumulated. Thus, these minerals were excluded from the list of candidate buffers. The kinetic constants k_{H^+} and k_W for these minerals were less than 10^{-8} and 10^{-11} mol m⁻² s⁻¹, respectively. Among the remaining eight minerals, $t_{99\%}$ varied from 21 days (nepheline) to 54 days (andradite). The minerals with smaller $t_{99\%}$ (<30 days), namely nepheline, fayalite, glaucophane, and lizardite, are the best candidates as acid-neutralizing agents. This result is partially corroborated by Kleiv and Sandvik (2000), who recognized the buffering properties of nepheline. The amount of mineral consumed to buffer the same amount of PCE was also computed (Table 7). Only relatively small variations were found, ranging from 0.32 to 0.97 g mineral consumed per mmol of PCE transformed. According to simulation results, dechlorination of 1.5 mmol of PCE will consume 0.7 to 1.5 g l⁻¹ of mineral for a period of approximately 1 month, depending on the mineral used.

4 Summary and Conclusions

The importance of groundwater pH control for enhanced in situ bioremediation of CAHs as well as other remediation technologies is well recognized. A batch biogeochemical model was implemented to evaluate the use of silicate minerals as buffering agents during the treatment of contaminated sites. To the best of our knowledge, this is the first study focusing on the use of silicate mineral powder in aquifers. Although in this work, the technology was applied to the specific case of CAH bioremediation, the geochemical model could be applied to other remediation processes requiring maintenance of neutral pH. As it stands, the model can be used as a design tool to calculate the amount of mineral needed. This requires the knowledge of the initial mass of CAHs.

Eight potentially suitable minerals were identified through the screening methodology. The other silicate minerals were excluded as their dissolution kinetic was too low to neutralize the acidity produced by the biological processes. The most promising candidate was nepheline, due to its relatively rapid dissolution rate. This result extends the work of Kleiv and Sandvik (2000), who proposed its use as buffering agent for heavy metal stabilization. The minerals considered in this study can be easily found on the market, as they are used in industrial processes (such as glass making, ceramics, abrasive) or in mine tailings, and are therefore relatively inexpensive. In the context of field application, the local availability of the mineral should also be assessed. The minerals considered in this study are distributed worldwide and mineralogical databases (e.g., www.mindat.org) can be used to identify local deposits and availability. For this reason, a detailed evaluation of the treatment costs, although important, is site specific and was beyond the scope of this study.

A sensitivity analyses was conducted to identify the parameters that control the model response and therefore need accurate characterization. It was observed that the most influential parameters are the mineral dissolution rate constants in the acidic and neutral ranges, k_{H^+} and k_W , the reaction order for protons promoted dissolution, n_{H^+} , and the solubility constant K_D . Due to the large uncertainties associated with the determination of the kinetic rate constants, the results of the sensitivity analysis suggested that model predictions should be further verified. Groundwater temperature is also important, as it controls both the rate of acidity production and the buffering capacity of the mineral.

The model includes the main geochemical and microbial processes that control pH evolution. Interactions between minerals and microorganisms were, however, neglected due to the lack of reliable data. Possible feedbacks include the microbial enhancement of mineral weathering rates (Barker et al. 1998; Ullman et al. 1996; Vandevivere et al. 1994) and the inhibition of bacteria by trace elements release during mineral dissolution (Dopson et al. 2008). The other important process not included in the model is the possible passivation of the mineral reactive surface due to secondary phase precipitation, which would decrease the dissolution rate and buffering capacity. Microcosm experiments are currently being conducted to validate the model and ascertain the importance of the different modeling assumptions.

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